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# Biotic stoichiometric controls on the deep ocean N:P ratio<sup>\*</sup>

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## Abstract

We re-examine what controls the deep ocean N:P ratio in the light of recent findings that the C:N:P stoichiometry of phytoplankton varies with growth rate, nutrient and light limitation, species and phylum, and that N<sub>2</sub>-fixation may be limited by Fe or light in large parts of the world ocean. In particular, we assess whether a systematic change in phytoplankton stoichiometry can alter the deep ocean N:P ratio. To do this we adapt recent models to include non-Redfieldian stoichiometry of phytoplankton and restriction of N<sub>2</sub>-fixers to a fraction of the surface ocean. We show that a systematic change in phytoplankton C:N:P can alter the concentrations of NO<sub>3</sub> and PO<sub>4</sub> in the deep ocean but cannot greatly alter their ratio, unless it also alters the N:P threshold for N<sub>2</sub>-fixation. This occurs if competitive dynamics set the N:P threshold for N<sub>2</sub>-fixation, in which case it remains close to the N:P requirement of non-fixers (rather than that of N<sub>2</sub>-fixers) and consequently so does the deep ocean N:P ratio. Then, even if N<sub>2</sub>-fixers are restricted to a fraction of the surface ocean, they reach higher densities there, minimising variations in deep ocean N:P. Theoretical limits on the N:P requirements of phytoplankton suggest that since the deep ocean became well oxygenated, its N:P ratio is unlikely to have varied by more than a factor of two in either direction. Within these bounds, evolutionary changes in phytoplankton composition, and increased phosphorus weathering due to the biological colonisation of the land surface, are predicted to have driven long-term changes in ocean composition.

## 1 Introduction

There is a well-known correspondence between the average proportions of N and P in marine organic matter – the “Redfield ratio” of N:P~16 – and the composition of the deep ocean with N:P~15. Redfield (1934) suggested that an explanation “... may be sought in the activities of those bacteria which form nitrogenous compounds or liberate nitrogen in the course of the decomposition of organic matter” intuiting that “... in a

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world populated by organisms of these two types the relative proportion of phosphate and nitrate must tend to approach that characteristic of protoplasm in general. . .” In his later work, Redfield (1958) proposed that: “When living in an environment containing a deficiency of nitrate relative to phosphate, the growth and assimilation of the nitrogen-fixing organisms might tend continually to bring the proportions of nitrogen and phosphorus nearer to that characteristic of their own substance.” Subsequent workers (Broecker and Peng, 1982; Tyrrell, 1999; Lenton and Watson, 2000) have expressed the mechanism in terms of competition between  $N_2$ -fixing organisms that are selected when  $N:P < 16$  and non-fixers that out-compete them when  $N:P > 16$ . This mechanism assumes that under P-limiting conditions  $N_2$ -fixers have a lower growth rate than non-fixers, because of the high energy cost of  $N_2$ -fixation, whilst under sufficiently N-limiting conditions  $N_2$ -fixers out-compete non-fixers.

The canonical value of  $\sim 16$  for the N:P Redfield ratio represents an average for today’s phytoplankton. It has long been known that the Redfield ratios of phytoplankton vary with growth rate (Goldman et al., 1979) and light regime (Goldman, 1986). Nutrient replete phytoplankton cultures (with consequently high growth rates) have a mean N:P of 10.1 across 34 studies, in contrast to marine particulate matter with a mean N:P of 16.4 across 27 studies (Geider and La Roche, 2002). It was thought that  $N:P \sim 16$  might represent some kind of optimum for phytoplankton, but no theoretical basis has yet been found for this (Klausmeier et al., 2004). Instead, a model predicts that the optimum composition of phytoplankton under exponential growth is 8.2, whilst under light limitation it is 35.8, nitrogen limitation 37.4, and phosphorus limitation 45.0 (Klausmeier et al., 2004). Furthermore, different phyla or super-families of differing antiquity have different N:P, with older “greens” having higher N:P than younger “reds” (Quigg et al., 2003). This raises the question (Falkowski and Davis, 2004; Arrigo, 2005): Would a systematic shift in the Redfield ratios alter deep ocean composition?

The question provokes a deeper one: What sets the deep ocean N:P ratio? Some authors still make statements, which can be traced back to Redfield (1934), to the effect that the ratio of major nutrients  $N:P \sim 15$  in the deep ocean directly reflects the

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average Redfield ratio (N:P~16) of sinking organic matter being remineralised in the water column. However, the cycle of uptake in the surface ocean and remineralisation at depth only redistributes  $\text{NO}_3$  and  $\text{PO}_4$ , it cannot directly alter their absolute or relative amounts in the ocean as a whole, which depend on net input to or removal from the ocean. The ocean mixing time ( $<10^3$  yr) is shorter than the residence time of  $\text{NO}_3$  ( $\sim 3 \times 10^3$  yr) (Codispoti, 1995; Lenton and Watson, 2000), which is in turn shorter than that of  $\text{PO}_4$  ( $\sim 1.8 \times 10^4$  yr) (Ruttenberg, 1993; Lenton and Watson, 2000). Hence mixing tends to homogenize the concentrations of both nutrients. Furthermore, we can consider a timescale over which  $\text{PO}_4$  is relatively constant but  $\text{NO}_3$  can vary due to imbalances of input (primarily  $\text{N}_2$ -fixation) and output (primarily denitrification) processes. The essence of Redfield's mechanism is that  $\text{N}_2$ -fixation responds to any deficit of  $\text{NO}_3$  relative to the N:P requirement of average phytoplankton (non-fixers), whilst denitrification tends to continually remove  $\text{NO}_3$  and thus maintain a small N:P deficit and corresponding population of  $\text{N}_2$ -fixers.

Both  $\text{N}_2$ -fixation and denitrification processes need some elaboration in the light of recent discoveries. On the input side, although  $\text{N}_2$ -fixation is sometimes P-limited and suppressed by N-addition, there is also evidence for Fe-limitation (Berman-Frank et al., 2001; Mills et al., 2004), light-limitation (Hood et al., 2004) and P and Fe co-limitation (Mills et al., 2004) of  $\text{N}_2$ -fixers. This raises the question: Given that  $\text{N}_2$ -fixers may be limited to restricted areas of the world ocean, can they still regulate deep ocean N:P? On the output side, anaerobic ammonium oxidation ("anammox";  $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ), in the ocean water column and sediments, has been found to be responsible for significant removal (up to 30–50%) of fixed nitrogen (Dalsgaard et al., 2003; Kuypers et al., 2003) and thus contributes to lowering deep ocean N:P. However, both processes occur under anaerobic conditions, and the nitrite ( $\text{NO}_2^-$ ) used in the anammox reaction may be supplied by denitrification (of  $\text{NO}_3$ ). Hence there is no qualitative change to Redfield's mechanism and in the remainder of this article we take 'denitrification' to also include anammox.

Our aims in this paper are to elucidate the controls on the deep ocean N:P ratio

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by adapting two existing, simple models (Tyrrell, 1999; Lenton and Watson, 2000) and conducting a series of “What if...?” thought experiments. Section 2 introduces the models and Sect. 3 presents the results. First we examine what controls deep ocean N:P by decoupling the N:P ratio of phytoplankton from the N:P threshold that triggers N<sub>2</sub>-fixation, and varying each independently. Having established which exerts the greatest control on deep ocean N:P, we couple these ratios through the common assumption that competitive dynamics set the N:P threshold for N<sub>2</sub>-fixation, and we maintain this assumption for the remainder of the Results. We examine the relative influences of the N:P ratios of non-fixers and of N<sub>2</sub>-fixers on the deep ocean N:P ratio. Then we consider what happens if N<sub>2</sub>-fixers are limited to a fraction of the surface ocean. The effects of changes in the N:P ratio of the phytoplankton (and corresponding changes in the N:P threshold of N<sub>2</sub>-fixation) on long-term steady state deep ocean N:P are estimated. Then the effect of variations in weathering rate are examined. Finally the combined effects of changes in N:P of the phytoplankton and changes in weathering are estimated over evolutionary timescales. Section 4 discusses the findings and Sect. 5 concludes.

## 2 Methods

Here we introduce the two models adapted for this study (Fig. 1–2). For further explanation and justification of their formulation see Lenton and Watson (2000) (henceforth LW) and Tyrrell (1999) (henceforth TT). Those readers familiar with one or both models may skip the corresponding section(s). Both are simple box models, LW is essentially a 1-box model, TT is a 2-box model and we extend it to 3 boxes. LW include N, P, C and O<sub>2</sub> cycling and concentrate on the feedback mechanisms in the system, but have no explicit biological populations. TT includes N and P cycling and explicit competition between N<sub>2</sub>-fixers and non-fixers, but has no C or O<sub>2</sub> cycling hence the effects of changes in C:P or C:N ratios cannot be addressed. Table 1 lists the key parameters varied in this study and all other model constants.

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## 2.1 LW model

Lenton and Watson (2000) model (Fig. 1) reservoirs of nitrate ( $\text{NO}_3$ , actually available nitrogen) and phosphate ( $\text{PO}_4$ ) expressed as deep ocean concentrations, and a reservoir of atmospheric oxygen ( $\text{O}_2$ ) expressed as the concentration in water ventilating the deep ocean. Here we generalize the original model (M1) of LW to allow independent variation of the C:N and C:P Redfield ratios of new production, denoted  $r_{\text{C:N}}$  and  $r_{\text{C:P}}$ , and the N:P threshold below which  $\text{N}_2$ -fixation occurs, denoted  $r_{\text{N:P,Fix}}$ .

The limiting nutrient in water up-welled to the surface ocean is assumed to be completely used up, generating a corresponding concentration ( $\mu\text{mol kg}^{-1}$ ) of carbon due to new production in the surface layer, denoted  $C$  here instead of  $N$  (to avoid confusion with Tyrrell's  $N$ ):

$$C = \min(r_{\text{C:N}}\text{NO}_3, r_{\text{C:P}}\text{PO}_4) \quad (1)$$

$\text{N}_2$ -fixation (N-Fix) is assumed to depend on the deficit of  $\text{NO}_3/r_{\text{N:P,Fix}}$  below  $\text{PO}_4$ :

$$F_{\text{N-Fix}} = \frac{k_3}{k_P} \left( \text{PO}_4 - \frac{\text{NO}_3}{r_{\text{N:P,Fix}}} \right) \quad (2)$$

where  $F$  denotes a flux. All constants are retained including the initial  $\text{N}_2$ -fixation flux  $k_3 = 8.7 \times 10^{12} \text{ mol N yr}^{-1}$  and the initial average deep ocean nutrient concentrations of  $\text{PO}_{4(0)} = 2.2 \mu\text{mol kg}^{-1}$  and  $\text{NO}_{3(0)} = 30.9 \mu\text{mol kg}^{-1}$  from World Ocean Atlas data. The derived constant  $k_P = \text{PO}_{4(0)} - \text{NO}_{3(0)}/16 = 0.26875 \mu\text{mol kg}^{-1}$  represents the surplus  $\text{PO}_4$  remaining in surface waters after  $\text{NO}_3$  has been removed by new production.  $\text{N}_2$ -fixation provides negative feedback on nitrate that tends to couple it to phosphate, e.g. increased  $\text{NO}_3$  suppresses  $\text{N}_2$ -fixation, counteracting the initial change.

The anoxic fraction of the ocean ( $A$ ) depends on the balance of oxygen supply via ocean mixing and oxygen demand due to respiration of sinking new production:

$$A = 1 - k_1 \frac{\text{O}_2}{\text{O}_{2(0)}} \frac{C_0}{C} \quad (3)$$

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The initial oxic fraction  $k_1=0.86$  and the initial anoxic fraction  $A_0=0.14$ . The initial oxygen concentration for water ventilating the deep ocean  $O_{2(0)}=331.5 \mu\text{mol kg}^{-1}$ , and the initial average carbon concentration due to new production in surface waters  $C_0=226.0 \mu\text{mol kg}^{-1}$ .

- 5 Denitrification (De-N) comprises a fixed sedimentary flux and a variable water column flux that depends on anoxia:

$$F_{\text{De-N}} = k_4 \left( 1 + \frac{A}{A_0} \right) \quad (4)$$

- where  $k_4=4.3 \times 10^{12} \text{ mol N yr}^{-1}$  is the initial size of each flux. The dependence of water column denitrification on anoxia provides negative feedback on nitrate that tends to couple nitrate to oxygen, e.g. increased  $\text{NO}_3$  increases new production, anoxia, and denitrification, thus counteracting the initial change.

A further minor sink of nitrate is organic nitrogen (Org-N) burial, which occurs with the burial of organic carbon and a C:N burial ratio  $b_{\text{C:N}}=37.5$ :

$$F_{\text{Org-N}} = \frac{k_2}{b_{\text{C:N}}} \left( \frac{C}{C_0} \right)^2 \quad (5)$$

- 15 where the initial organic carbon burial flux  $k_2=3.75 \times 10^{12} \text{ mol C yr}^{-1}$ , hence organic nitrogen burial is initially  $0.1 \times 10^{12} \text{ mol N yr}^{-1}$ . Organic nitrogen burial provides a small additional negative feedback on nitrate, e.g. increased  $\text{NO}_3$  increases new production and Org-N burial, thus counteracting the initial change.

The overall rate of change of nitrate is given by:

$$20 \frac{d\text{NO}_3}{dt} = k_8 (F_{\text{N-Fix}} - F_{\text{De-N}} - F_{\text{Org-N}}) \quad (6)$$

where  $k_8=7.1 \times 10^{-22} \text{ kg}^{-1}$  converts from reservoir size in mol to average concentration. The overall balance of feedbacks is such that nitrate tracks any variations in phosphate.

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Normalized weathering,  $W$ , represents the only external forcing parameter for the model (i.e.  $W=1$  at present day). Weathering drives phosphorus input to the ocean (P-in), via rivers:

$$F_{P-in} = k_5 W \quad (7)$$

- 5 with initial flux  $k_5=3.6 \times 10^{10} \text{ mol P yr}^{-1}$ . Phosphorus is removed from the ocean via burial in sediments, which occurs in three main forms:

Burial of phosphorus with iron oxides (Fe-P) is initially  $k_6=0.6 \times 10^{10} \text{ mol P yr}^{-1}$  and is inversely dependent on anoxia:

$$F_{Fe-P} = \frac{k_6}{k_1} (1 - A) \quad (8)$$

- 10 This provides a positive feedback on phosphate, e.g. increased  $\text{PO}_4$  tends to increase  $\text{NO}_3$ , new production and anoxia, decreasing Fe-P burial and tending to further increase  $\text{PO}_4$ .

Organic phosphorus (Org-P) burial is initially  $1.5 \times 10^{10} \text{ mol P yr}^{-1}$  and occurs with the burial of organic carbon in a C:P burial ratio  $b_{C:P}=250$ :

$$15 \quad F_{Org-P} = \frac{k_2}{b_{C:P}} \left( \frac{C}{C_0} \right)^2 \quad (9)$$

The dependence on new production provides negative feedback on phosphate, e.g. increased  $\text{PO}_4$  tends to increase  $\text{NO}_3$ , new production and Org-P burial, thus counter-acting the initial change.

- 20 Calcium-bound (Ca-P) phosphorus burial is also initially  $k_7=1.5 \times 10^{10} \text{ mol P yr}^{-1}$  and is largely authigenic (it forms in sediments). The phosphorus buried as Ca-P is supplied via new production hence it has the same functional dependence on new production as Org-P burial:

$$F_{Ca-P} = k_7 \left( \frac{C}{C_0} \right)^2 \quad (10)$$

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This provides further negative feedback on phosphate.

The overall rate of change of phosphate is given by:

$$\frac{d\text{PO}_4}{dt} = k_8 (F_{\text{P-in}} - F_{\text{Fe-P}} - F_{\text{Org-P}} - F_{\text{Ca-P}}) \quad (11)$$

The overall feedback is negative tending to buffer variations in phosphate, e.g. those driven by changes in weathering.

Organic carbon (Org-C) burial provides the net source of atmospheric oxygen and depends quadratically on new production:

$$F_{\text{Org-C}} = k_2 \left( \frac{C}{C_0} \right)^2 \quad (12)$$

Although Org-C burial has no direct dependence on oxygen, the dependence of Fe-P burial on anoxia provides a negative feedback on atmospheric oxygen, e.g. increased  $\text{O}_2$  decreases anoxia, increasing Fe-P burial, decreasing  $\text{PO}_4$ , tending to decrease new production and Org-C burial, thus counteracting the initial change.

Oxidative weathering (Ox-W) provides the net sink of atmospheric oxygen and is forced by  $W$ :

$$F_{\text{Ox-W}} = k_2 W \quad (13)$$

All reduced material that is exposed is assumed to be oxidized, thus making oxygen consumption independent of oxygen level.

The overall rate of change of oxygen is given by:

$$\frac{d\text{O}_2}{dt} = k_9 (F_{\text{Org-C}} - F_{\text{Ox-W}}) \quad (14)$$

where  $k_9 = 8.96 \times 10^{-24} \text{ kg}^{-1}$  converts from atmospheric oxygen reservoir size in mol to concentration dissolved in surface waters ventilating the deep ocean. Atmospheric oxygen has a much longer response time to perturbations ( $\approx 10^7$  yr) than either of the

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nutrient reservoirs. Hence the steady state response to variations in  $W$  is achieved over a much longer timescale than the steady state response to variations in  $r_{C:N}$ ,  $r_{C:P}$  or  $r_{N:P,Fix}$ , none of which affect  $O_2$ .

5 The system was solved analytically for steady state following the method in the Appendix of LW but for an unknown limiting nutrient, yielding:

$$\frac{C}{C_0} = W^{\frac{1}{2}} \quad (15)$$

$$\frac{O_2}{O_{2(0)}} = W^{\frac{3}{2}} \quad (16)$$

$$A = 1 - k_1 W \quad (17)$$

$$PO_4 = \frac{NO_3}{r_{N:P,Fix}} + k_P (4.025 - 3.025W) \quad (18)$$

10 Steady state for  $O_2$  is lost when  $A \rightarrow 0$ , which from Eq. (17) gives an upper limit on  $W = 1.163$  (above this,  $O_2$  increases monotonically). From Eqs. (1) and (15):

$$\min(r_{C:N}NO_3, r_{C:P}PO_4) = C_0 W^{\frac{1}{2}} \quad (19)$$

which determines the value of the limiting nutrient and the other nutrient is found from Eq. (18). When  $NO_3$  is limiting:

$$15 \quad NO_3 = \frac{C_0 W^{\frac{1}{2}}}{r_{C:N}} \quad (20)$$

$$PO_4 = \frac{C_0 W^{\frac{1}{2}}}{r_{C:N}r_{N:P,Fix}} + k_P (4.025 - 3.025W) \quad (21)$$

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When  $\text{PO}_4$  is limiting:

$$\text{PO}_4 = \frac{C_0 W^{\frac{1}{2}}}{r_{\text{C:P}}} \quad (22)$$

$$\text{NO}_3 = r_{\text{N:P,Fix}} \left( \frac{C_0 W^{\frac{1}{2}}}{r_{\text{C:P}}} - k_P (4.025 - 3.025W) \right) \quad (23)$$

LW took  $r_{\text{C:N}}=117/16=7.3125$  and  $r_{\text{C:P}}=117$  from nutrient data analysis (Anderson and Sarmiento, 1994) and assumed  $r_{\text{N:P,Fix}}=r_{\text{C:P}}/r_{\text{C:N}}=16$ , hence  $\text{NO}_3$  was always limiting. This corresponds to a steady state  $\text{PO}_4=2.2 \mu\text{mol kg}^{-1}$  and  $\text{NO}_3=30.9 \mu\text{mol kg}^{-1}$ , i.e. deep ocean N:P=14.0 (a little below observations).

## 2.2 Extended TT model

Tyrrell (1999) models nitrate and phosphate in two boxes, the surface and deep ocean, and includes explicit competition between  $\text{N}_2$ -fixing and non-fixing organisms in the surface ocean. Here we extended the TT model (Fig. 2) in two ways: First, nitrogen-fixers and other phytoplankton are given different N:P stoichiometry ( $R_{\text{NF}}$  and  $R_{\text{O}}$  respectively). Second, the surface layer of the ocean is split into two boxes, a fraction where nitrogen-fixers can grow ( $f_A$ ) and a fraction where they cannot ( $f_B=1-f_A$ ), due to limitation by e.g. iron or light. These two boxes are not directly coupled, but both exchange nutrients and dead biomass with the deep layer. The subscripts  $A$ ,  $B$  and  $D$  refer to the two surface boxes and the deep box, respectively.  $\text{NF}$  is the standing stock of  $\text{N}_2$ -fixers and  $\text{O}$  that of other phytoplankton.  $P$  and  $N$  are the concentrations of  $\text{PO}_4$  and  $\text{NO}_3$ , respectively. All other symbols and parameter values are as in Tyrrell (1999).

The dynamics of each population is determined by a balance of nutrient uptake and mortality, described by:

$$\frac{d\text{NF}_A}{dt} = \mu'_{\text{NF}} \cdot \frac{P_A}{P_A + P_H} \cdot \text{NF}_A - M \cdot \text{NF}_A \quad (24)$$

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$$\frac{dO_A}{dt} = \mu'_O \cdot \min \left( \frac{P_A}{P_A + P_H}, \frac{N_A}{N_A + N_H} \right) \cdot O_A - M \cdot O_A \quad (25)$$

$$\frac{dO_B}{dt} = \mu'_O \cdot \min \left( \frac{P_B}{P_B + P_H}, \frac{N_B}{N_B + N_H} \right) \cdot O_B - M \cdot O_B \quad (26)$$

where net primary production of nitrogen fixers is limited only by  $P$ , following Michaelis-Menten kinetics with a half-saturation constant,  $P_H = 3 \times 10^{-5} \text{ mol P m}^{-3}$  and maximum growth rate,  $\mu'_{NF} = 87.6 \text{ yr}^{-1}$ . Other phytoplankton can be limited by either  $N$  or  $P$ , with half-saturation constant for growth on  $N$  of  $N_H = 5 \times 10^{-4} \text{ mol N m}^{-3}$ , and a higher maximum growth rate of  $\mu'_O = 91.25 \text{ yr}^{-1}$ . Mortality for both types of plankton,  $M = 73 \text{ yr}^{-1}$ .

$N_2$ -fixers are given a lower maximum growth rate on  $P$  because of the energy demands of  $N_2$ -fixation. Thus if  $P$  is limiting they are out-competed, but this removes a source of  $N$  to the system, and  $N$  drops until the system settles into an  $N$ -limited state. In that state, there is negative feedback on changes in  $N$  – should  $N$  increase,  $N_2$ -fixers will tend to be out-competed by other plankton, conversely, should  $N$  drop,  $N_2$ -fixers tend to make up a larger fraction of the population.

The model schematic (Fig. 2) illustrates the key fluxes of both nutrients.  $N$  and  $P$  are removed from the surface boxes by biological uptake, but for both nutrients,  $SR = 95\%$  of total primary productivity is regenerated in the surface layer.  $N$  is fixed from outside the system directly into  $N_2$ -fixers, and enters box  $A$  via their mortality and remineralisation.  $N$  is removed from the system by denitrification, with  $DN = 1.5\%$  of total  $N$  uptake converted to  $N_2$  via denitrification, 75% of this in the surface layer. Mixing of water ( $K = 3.0 \text{ m yr}^{-1}$ ) with the deep box provides a net input of nutrients to each surface box.  $N$  also enters the surface boxes from rivers ( $RN = 6.0 \times 10^{-3} \text{ mol N m}^{-2} \text{ yr}^{-1}$ ) and atmospheric deposition ( $AN = 7.5 \times 10^{-3} \text{ mol N m}^{-2} \text{ yr}^{-1}$ ), whilst  $P$  enters only from rivers ( $RP = 2.0 \times 10^{-4} \text{ mol P m}^{-2} \text{ yr}^{-1}$ ). All these fluxes determine the rate of change of

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nutrient concentrations in the surface ocean boxes, described by:

$$\begin{aligned} \frac{dP_A}{dt} = & -\mu'_{NF} \cdot \frac{P_A}{P_A+P_H} \cdot \frac{NF_A}{R_{NF}} \\ & -\mu'_O \cdot \min\left(\frac{P_A}{P_A+P_H}, \frac{N_A}{N_A+N_H}\right) \cdot \frac{O_A}{R_O} \\ & +M \cdot SR \cdot \frac{NF_A}{R_{NF}} + M \cdot SR \cdot \frac{O_A}{R_O} \\ & + \frac{K \cdot (P_D - P_A)}{SD} + \frac{RP}{SD} \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{dN_A}{dt} = & -\mu'_O \cdot \min\left(\frac{P_A}{P_A+P_H}, \frac{N_A}{N_A+N_H}\right) \cdot O_A \\ & +M \cdot (SR - 0.75 \cdot DN) \cdot NF_A \\ & +M \cdot (SR - 0.75 \cdot DN) \cdot O_A \\ & + \frac{K \cdot (N_D - N_A)}{SD} + \frac{(RN+AN)}{SD} \end{aligned} \quad (28)$$

$$\begin{aligned} \frac{dP_B}{dt} = & -\mu'_O \cdot \min\left(\frac{P_B}{P_B+P_H}, \frac{N_B}{N_B+N_H}\right) \cdot \frac{O_B}{R_O} \\ & +M \cdot SR \cdot \frac{O_B}{R_O} + \frac{K \cdot (P_D - P_B)}{SD} + \frac{RP}{SD} \end{aligned} \quad (29)$$

$$\begin{aligned} \frac{dN_B}{dt} = & -\mu'_O \cdot \min\left(\frac{P_B}{P_B+P_H}, \frac{N_B}{N_B+N_H}\right) \cdot O_B \\ & +M \cdot (SR - 0.75 \cdot DN) \cdot O_B \\ & + \frac{K \cdot (N_D - N_B)}{SD} + \frac{(RN+AN)}{SD} \end{aligned} \quad (30)$$

where  $SD=500$  m is the depth of the surface layer.

Nutrients enter the deep ocean via remineralisation with  $DR=4.8\%$  of total primary productivity regenerated in the deep layer (leaving  $0.2\%$  to leave the system via burial in sediments). Denitrification ( $25\%$  of  $DN$ ) removes some  $N$  from the sinking flux.

There is also a net removal of both nutrients from the deep box due to mixing with the surface boxes. These fluxes determine the rate of change of nutrient concentrations in

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the deep ocean, given by:

$$\begin{aligned} \frac{dP_D}{dt} = & M \cdot DR \cdot \frac{NF_A}{R_{NF}} \cdot \frac{f_A \cdot SD}{DD} \\ & + M \cdot DR \cdot \frac{O_A}{R_O} \cdot \frac{f_A \cdot SD}{DD} \\ & + M \cdot DR \cdot \frac{O_B}{R_O} \cdot \frac{f_B \cdot SD}{DD} \\ & - \frac{K \cdot (P_D - f_A P_A - f_B P_B)}{DD} \end{aligned} \quad (31)$$

$$\begin{aligned} \frac{dN_D}{dt} = & M \cdot (DR - 0.25 \cdot DN) \cdot NF_A \cdot \frac{f_A \cdot SD}{DD} \\ & + M \cdot (DR - 0.25 DN) \cdot O_A \cdot \frac{f_A \cdot SD}{DD} \\ & + M \cdot (DR - 0.25 DN) \cdot O_B \cdot \frac{f_B \cdot SD}{DD} \\ & - \frac{K \cdot (N_D - f_A N_A - f_B N_B)}{DD} \end{aligned} \quad (32)$$

where  $DD=3230$  m is the depth of the deep layer.

Denitrification and N burial remove a constant fraction of the N taken up in net primary production from the system, providing a linear negative feedback on changes in  $N$ . P burial provides an equivalent linear negative feedback on changes in  $P$ .

Setting  $f_A=1$  and  $R_{NF}=R_O=16$  ( $=R_{ORG}$ ) recovers the original TT model. These equations were solved numerically with a Fortran program and using Mathematica software.

## 2.3 Application of the models

We use the two models in a complementary fashion. In the LW model, the distinction between the N:P ratio of the phytoplankton and the N:P threshold that triggers  $N_2$ -fixation allows us to first independently examine their influences on deep ocean N:P. These ratios are then equated in the LW model for the remainder of the Results. This assumes that competitive dynamics set the N:P threshold for  $N_2$ -fixation, which is implicit in the TT model. Under this assumption, we use both models to examine the effect of changes in phytoplankton N:P on deep ocean N:P. We use the extended TT model to further examine the relative impact of independently varying the N:P ratios of  $N_2$ -fixers

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and non-fixers, and the effect of restricting N<sub>2</sub>-fixers to a progressively smaller fraction of the surface ocean. Then we use the LW model to examine the effects of changes in C:P and C:N as well as N:P ratios of the phytoplankton, and the effect of changes in weathering. In all cases we concentrate on the steady state solutions of the models, rather than their transient responses. In response to changes in phytoplankton stoichiometry and/or the N:P threshold that triggers N<sub>2</sub>-fixation, steady state is achieved over 10<sup>4</sup>–10<sup>5</sup> yr, whereas in response to changes in weathering it takes 10<sup>6</sup>–10<sup>7</sup> yr.

### 3 Results

#### 3.1 What controls deep ocean N:P?

From the analytical solution of the LW model for steady state (Sect. 2.1) (valid for normalised weathering forcing  $0 \leq W \leq 1.163$ ), we find the following solutions for the ratio of available nitrogen (NO<sub>3</sub>) and phosphorus (PO<sub>4</sub>) in the deep ocean. When NO<sub>3</sub> is limiting:

$$\frac{\text{NO}_3}{\text{PO}_4} = \left( \frac{1}{r_{\text{N:P,Fix}}} + \frac{r_{\text{C:N}} k_P}{C_0 W^{\frac{1}{2}}} (4.025 - 3.025W) \right)^{-1} \quad (33)$$

When PO<sub>4</sub> is limiting:

$$\frac{\text{NO}_3}{\text{PO}_4} = r_{\text{N:P,Fix}} \left( 1 - \frac{r_{\text{C:P}} k_P}{C_0 W^{\frac{1}{2}}} (4.025 - 3.025W) \right) \quad (34)$$

The condition for NO<sub>3</sub> to be limiting is:

$$\frac{1}{r_{\text{C:P}}} - \frac{1}{r_{\text{C:N}} r_{\text{N:P,Fix}}} \leq \frac{k_P}{C_0 W^{\frac{1}{2}}} (4.025 - 3.025W) \quad (35)$$

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For the default parameter values,  $\text{NO}_3$  is limiting. However, if the N:P threshold that triggers  $\text{N}_2$ -fixation ( $r_{\text{N:P,Fix}}$ ) and the N:P Redfield ratio ( $r_{\text{N:P}}$ ) can be decoupled, then  $\text{PO}_4$  limitation can be triggered by increasing  $r_{\text{N:P,Fix}}$ , or by decreasing  $r_{\text{N:P}}$  (by either decreasing  $r_{\text{C:P}}$  or by increasing  $r_{\text{C:N}}$ ).

5 Figures 3 and 4 show, for present day weathering  $W=1$ , the effects of independently varying  $r_{\text{N:P,Fix}}$ ,  $r_{\text{C:P}}$ , or  $r_{\text{C:N}}$  on  $\text{NO}_3/r_{\text{N:P}}$ ,  $\text{PO}_4$ , and the deep ocean N:P ratio. With fixed  $W=1$ , atmospheric oxygen, new production, and ocean anoxia are constant at their initial values (from Eqs. 15–17).

Deep ocean N:P is primarily controlled by the N:P threshold that triggers  $\text{N}_2$ -fixation,  $r_{\text{N:P,Fix}}$  (Fig. 3). Considering Eqs. 33 and 34,  $k_P=0.26875 \mu\text{mol kg}^{-1}$  is small, therefore  
 10 deep ocean N:P is set modestly below  $r_{\text{N:P,Fix}}$ , whether N or P is limiting. In mechanistic terms, denitrification in the water column and sediments, plus a small amount of organic nitrogen burial, continually remove N from the ocean, thus lowering deep ocean N:P and supporting a counter-balancing flux of  $\text{N}_2$ -fixation. For the default parameter  
 15 values shown, in the N-limiting regime, deep ocean N:P tends toward  $r_{\text{N:P,Fix}}$  as  $r_{\text{N:P,Fix}}$  tends to zero. When  $r_{\text{N:P,Fix}}$  is increased, this tends to transiently increase  $\text{N}_2$ -fixation,  $\text{NO}_3$ , new production, Org-P and Ca-P burial until steady state is restored with lower  $\text{PO}_4$ , identical  $\text{NO}_3$  and consequently higher deep ocean N:P. When  $r_{\text{N:P,Fix}} \geq 18.6$ , a switch to P-limitation occurs. Now as  $r_{\text{N:P,Fix}}$  is increased further, increases in  $\text{N}_2$ -  
 20 fixation increase steady-state  $\text{NO}_3$  (because it is no longer limiting) without affecting  $\text{PO}_4$  (which remains constant). Thus deep ocean  $\text{N:P}=0.86 r_{\text{N:P,Fix}}$  increases linearly.

When the N:P threshold triggering  $\text{N}_2$ -fixation is fixed at  $r_{\text{N:P,Fix}}=16$ , varying the N:P Redfield ratio – by varying either C:P or C:N – has little effect on the deep ocean N:P ratio (Fig. 4), although the concentrations of  $\text{NO}_3$  and  $\text{PO}_4$  can be substantially altered.

25 When varying  $r_{\text{C:P}}$  with fixed  $r_{\text{C:N}}=7.3125$  (Fig. 4a), if the system is in the N-limiting regime, deep ocean N:P ratio remains constant at 14.04 ( $r_{\text{C:P}}$  does not appear in Eq. 33). Indeed the concentrations of both nutrients are constant (Eqs. 20–21) because changes in C:P do not alter any of the controlling fluxes when N is limiting and C:N is constant. If  $r_{\text{C:P}} \leq 102.7$  (corresponding to  $r_{\text{N:P}} \leq 14.04$ ), a switch to P-limitation

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occurs. Further decreases in  $r_{C:P}$  transiently reduce new production, Org-P burial, Ca-P burial, Org-N burial, anoxia and denitrification until steady state is restored with higher concentrations of both  $\text{NO}_3$  and  $\text{PO}_4$ . Deep ocean N:P increases linearly with decreasing  $r_{C:P}$ , tending toward  $r_{N:P,\text{Fix}}=16$  as  $r_{C:P}$  tends toward zero.

5 When varying  $r_{C:N}$  with fixed  $r_{C:P}=117$  (Fig. 4b), in the N-limiting regime, deep ocean N:P ratio shows a weak sensitivity to  $r_{C:N}$  (Eq. 33). As  $r_{C:N}$  is decreased (corresponding to increasing  $r_{N:P}$ ), deep ocean N:P tends toward  $r_{N:P,\text{Fix}}$ . As  $r_{C:N}$  is increased, transient increases in new production, Org-P burial, Ca-P burial, Org-N burial, anoxia and denitrification give rise to a new steady state with lower concentrations of both  $\text{NO}_3$  and  $\text{PO}_4$ . If  $r_{C:N} \geq 8.49$  (corresponding to  $r_{N:P} \leq 13.77$ ), a switch to P-limitation occurs. In this regime,  $r_{C:N}$  has no effect on either  $\text{NO}_3$  or  $\text{PO}_4$  (Eqs. 22–23) and deep ocean N:P is constant at 13.77.

Thus, a systematic change in phytoplankton C:N:P stoichiometry can alter the concentrations of  $\text{NO}_3$  and  $\text{PO}_4$  in the deep ocean but cannot greatly alter their ratio, unless it also alters the N:P threshold for  $\text{N}_2$ -fixation. This is a useful insight from the model, particularly if in reality  $r_{N:P}$  and  $r_{N:P,\text{Fix}}$  can be decoupled. However, it may be of limited applicability to the real ocean, because (as we will assume for the remainder of the Results section) changes in the N:P requirement of the phytoplankton are expected to alter the N:P threshold for  $\text{N}_2$ -fixation. In particular, it is implicit in Redfield's (1958) mechanism that the N:P level triggering  $\text{N}_2$ -fixation cannot be decoupled from the N:P ratio of the phytoplankton because the latter sets the threshold below which  $\text{N}_2$ -fixers are selected and  $\text{N}_2$ -fixation occurs. This can be explained in terms of competitive dynamics (Schade et al., 2005): If the N:P supply ratio in the water is below the N:P requirement of non-fixers, then they will use up all the N and leave some P remaining.  $\text{N}_2$ -fixers can utilise this P and in so doing add fixed N to the system. This will continue until the N:P supply ratio approaches the N:P requirement of the non-fixers, at which point the  $\text{N}_2$ -fixers tend to be out-competed because  $\text{N}_2$ -fixation is an energy demanding process.

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### 3.2 Assuming competitive dynamics set the N:P threshold for N<sub>2</sub>-fixation

In the LW model, if we assume that the average N:P ratio of the phytoplankton is the N:P ratio that triggers N<sub>2</sub>-fixation (i.e.  $r_{N:P,Fix}=r_{C:P}/r_{C:N}=r_{N:P}$ ), then  $NO_3=C_0/r_{C:N}$  is always limiting,  $PO_4=(C_0/r_{C:P})+k_P$  and deep ocean N:P:

$$\frac{NO_3}{PO_4} = r_{N:P} \left( \frac{1}{1 + r_{C:P}k_P/C_0} \right) \quad (36)$$

In the original TT model this assumption is implicit because competition between N<sub>2</sub>-fixers and non-fixers is made explicit. They have identical N:P ratios ( $r_{N:P}=R_O=R_{NF}$ , which was  $R_{ORG}$  in TT's notation). N<sub>2</sub>-fixers are given a lower maximum growth rate on P because of the energy demands of N<sub>2</sub>-fixation. For the default parameter settings including a fixed weathering flux of P to the ocean, deep ocean  $PO_4=1.75 \mu\text{mol kg}^{-1}$  and the deep ocean N:P ratio:

$$\frac{NO_3}{PO_4} = \frac{(r_{N:P} \times 1.475) + 2}{1.75} \quad (37)$$

Hence in both models, if it is assumed that the N:P ratio of the phytoplankton ( $r_{N:P}$ ) determines the N:P threshold that triggers N<sub>2</sub>-fixation ( $r_{N:P,Fix}=r_{N:P}$  in LW), then the deep ocean N:P ratio will track changes in  $r_{N:P}$ , dropping further below it the more  $r_{N:P}$  is increased (Fig. 5). This is consistent with the direct dependence of deep ocean N:P on decoupled changes in the N:P threshold that triggers N<sub>2</sub>-fixation (Fig. 3) and may be contrasted with the insensitivity of deep ocean N:P to de-coupled changes in phytoplankton N:P (Fig. 4). In the TT model, deep ocean  $PO_4$  is fixed, which is equivalent to fixing the C:P Redfield ratio ( $r_{C:P}$ ) in the LW model. In both cases (Fig. 5), deep ocean N:P linearly tracks the phytoplankton N:P ratio entirely through changes in  $NO_3$ . The only difference between the models is in the default gradient (0.84 in TT, 0.88 in LW) and offset (1.14 in TT, 0 in LW) of the relationship.

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If the C:N Redfield ratio is fixed in the LW model, then  $\text{NO}_3$  is fixed and deep ocean N:P tracks phytoplankton N:P entirely through changes in  $\text{PO}_4$ . In this case, it is instructive to re-write Eq. (36) in the form:

$$\frac{\text{NO}_3}{\text{PO}_4} = \frac{r_{\text{N:P}}}{1 + r_{\text{N:P}} r_{\text{C:N}} k_P / C_0} \quad (38)$$

- 5 Now, the larger the N:P ratio of the phytoplankton, the further the deep ocean N:P ratio drops below it (Fig. 5). However, as  $r_{\text{C:N}} k_P / C_0$  is small, the offset is modest.

### 3.3 Relative effects of $\text{N}_2$ -fixer and non-fixer N:P

Our extension of the TT model to include different N:P ratios for  $\text{N}_2$ -fixers and non-fixers, allows us to examine their relative effects on the deep ocean N:P ratio.  $\text{N}_2$ -fixers often have a higher N:P ratio than non-fixers (Klausmeier et al., 2004) with reported N:P values for  $\text{N}_2$ -fixing *Trichodesmium* colonies ranging from 18.3 (Sañudo-Wilhelmy et al., 2001) to 125 (Karl et al., 1992). However, this should have little effect on the N:P of deep water, because the density of  $\text{N}_2$ -fixers is regulated by the N:P requirements of the non-fixers. Model results (Fig. 6) confirm this; for example, steady-state deep water N:P ratio is 14.6 when  $\text{N}_2$ -fixers have an N:P ratio of 16 and 14.7 when  $\text{N}_2$ -fixers have an N:P ratio of 125. In contrast, deep ocean N:P ratio varies linearly with the N:P ratio of non-fixers (Fig. 6). Thus, contrary to Redfield (1958) (as quoted in Sect. 1), it is the N:P ratio of non-fixers (rather than  $\text{N}_2$ -fixers) that sets the N:P threshold for  $\text{N}_2$ -fixation, which consequently determines the deep ocean N:P ratio.

### 3.4 What if $\text{N}_2$ -fixation is restricted to a fraction of the surface ocean?

If  $\text{N}_2$ -fixation is restricted to a progressively smaller fraction ( $f_A$ ) of the surface ocean, we find that deep ocean N:P is remarkably well regulated (Fig. 7). As  $f_A$  is reduced from 1 to 0.33, steady state deep ocean N:P declines from 14.6 to 11.5; for example, when only 50% of the ocean is available to  $\text{N}_2$ -fixers, deep N:P is 12.9. As  $f_A$  is reduced

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below 0.33, the system undergoes a Hopf bifurcation to an oscillating solution, and deep N:P actually increases, oscillating in the range 13.5–13.7 for  $f_A=0.329$ . As  $f_A$  is reduced further, deep N:P declines in a non-linear fashion; for example, when only 25% of the ocean is available to  $N_2$ -fixers, the deep N:P oscillates in the range 12.8–13.0, whereas when  $N_2$ -fixers are restricted to 15% of the surface ocean, deep N:P is still 11.5–11.7. As  $f_A$  tends to zero, deep ocean N:P also tends to zero, and in the absence of  $N_2$ -fixers, the oscillations disappear.

Such homeostatic control over the deep ocean N:P ratio is maintained in the model because  $N_2$ -fixers reach higher densities when restricted to smaller fractions of the ocean's surface, compensating for their reduced distribution. Although the predicted values of deep N:P fall below those observed, this is sensitive to the choice of model parameters. If we assume that the N:P Redfield ratio of non-fixers ( $R_O$ ) is somewhat greater than 16, this can compensate for restricting  $N_2$ -fixers to a fraction of the ocean's surface, for example, with  $f_A=0.5$ ,  $R_O=18$  recovers a deep ocean N:P=14.3.

### 3.5 What if the Redfield ratios change?

Theoretical limits on the N:P requirements of phytoplankton of 8.2–45.0 have been estimated (Klausmeier et al., 2004). Exponential growth favours greater allocation to P-rich assembly machinery and hence a lower N:P ratio. Competitive equilibrium favours greater allocation to P-poor resource-acquisition machinery and hence a higher N:P ratio. Whether light, N or P is limiting has a second-order effect, with P-limitation favouring the least allocation to assembly and the highest N:P ratio. We take the estimated limits from Klausmeier et al. (2004) as plausible bounds on the composition of the phytoplankton.

Corresponding limits on deep ocean N:P can be derived for the TT model and for the LW model assuming  $r_{N:P,Fix}=r_{N:P}$  with either fixed  $r_{C:P}$  or fixed  $r_{C:N}$  (Table 2 and Fig. 5). All three model variants give similar results. Fixed  $r_{C:N}$  in the LW model is the most defensible, because existing data indicate that phytoplankton C:N is less variable than N:P and C:P (Geider and La Roche, 2002; Quigg et al., 2003). This model variant

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suggests that deep ocean N:P has a maximum range of 7.7–32.3 (i.e. about a factor of 2 in either direction).

We can also use the LW model to consider the effect on ocean composition of systematic changes in the phytoplankton C:N:P over evolutionary time (Quigg et al., 2003), assuming that changes in phytoplankton N:P drove corresponding changes in the N:P threshold triggering  $N_2$ -fixation ( $r_{N:P,Fix}=r_{N:P}$ ). Table 3 shows the ocean composition predicted (from Eq. 36) if it were dominated by each of a series of phyla/super-families of decreasing antiquity. This suggests that a general decrease in N:P ratios of marine phytoplankton over the past ~1000 Myr would have tended to decrease deep ocean N:P. This is predicted to have occurred via increasing ocean  $PO_4$ , due to the general decrease in phytoplankton C:P, whereas the relative constancy of the phytoplankton C:N ratio would not have forced  $NO_3$ .

### 3.6 What if phosphorus weathering changes?

Thus far we have assumed weathering forcing ( $W$ ) is fixed, which has not been the case (Bergman et al., 2004; Lenton and Watson, 2004). The biological colonisation of the land surface has tended to accelerate weathering, in particular of phosphorus. This in turn has tended to increase atmospheric  $O_2$ . Retaining the dependence on weathering forcing in the LW model but assuming  $r_{N:P,Fix}=r_{N:P}$  gives:

$$\frac{NO_3}{PO_4} = r_{N:P} \left( 1 + \frac{r_{C:P} k_P}{C_0 W^{\frac{1}{2}}} (4.025 - 3.025W) \right)^{-1} \quad (39)$$

A general increase in weathering forcing ( $W$ ) toward the present, due to biotic colonisation of the land surface would have tended to increase deep ocean N:P (Fig. 8), bringing it closer to the N:P of the phytoplankton. The increase in deep ocean N:P occurs through a proportionally greater increase in  $NO_3$  than  $PO_4$ . The reason that  $NO_3$  drops more under decreased  $W$  than  $PO_4$  is that  $O_2$  drops and anoxia increases (Eqs. 16–17), and this both increases denitrification, lowering  $NO_3$ , and encourages

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Fe-P recycling from sediments, counteracting the decline in P input to the ocean.

### 3.7 Combined effects over evolutionary time

We have predicted that over the past ~1000 Myr, a decline in the N:P Redfield ratio and an increase in weathering forcing would have had counteracting effects on the deep ocean N:P ratio, the former tending to decrease it, the latter to increase it. However, their effects are mediated by different nutrients. A declining N:P Redfield ratio with relatively constant C:N tends primarily to increase  $\text{PO}_4$ , whereas an increase in weathering tends primarily to increase  $\text{NO}_3$ . The combined effect (given by Eq. 39) is rather complex, so let us consider an illustrative case: ~1000 Myr ago, we suggest  $W=0.5$ , and estimate C:N:P = 200:29:1 from averaging the values for Prasinophyceae and Chlorophyceae in Table 3 (Quigg et al., 2003). The predicted ocean composition is  $\text{NO}_3=23.2 \mu\text{mol kg}^{-1}$ ,  $\text{PO}_4=1.47 \mu\text{mol kg}^{-1}$ , and deep ocean N:P=15.7. The lower  $\text{NO}_3$  relative to the present day is due entirely to the lower weathering rates and the lower  $\text{PO}_4$  is due primarily to the estimated higher C:P of the phytoplankton (compare the result with the top entries in Table 3).

## 4 Discussion

As Redfield recognised, phytoplankton C:N:P=106:16:1 simply represents an average of the present phytoplankton community, there is as yet no evidence that it is optimal, and C:N:P is now known to vary with growth conditions, among species, and (probably) over evolutionary time. We find that the N:P ratio that triggers  $\text{N}_2$ -fixation sets the N:P ratio of the deep ocean (referring here to the average concentrations of N and P, not the proportions in which they are remineralised). Hence deep ocean N:P would be insensitive to changes in the N:P Redfield ratio of sinking material if there were no corresponding changes in the N:P threshold that triggers  $\text{N}_2$ -fixation. However, in reality all three N:P ratios are coupled: The N:P requirement of non-fixing phytoplankton

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determines the N:P threshold for N<sub>2</sub>-fixation, and this in turn sets deep ocean N:P. Furthermore, N<sub>2</sub>-fixation can be limited by Fe, light or other factors, such that N<sub>2</sub>-fixers are restricted to a modest fraction of the surface ocean, but they can still maintain deep ocean N:P relatively close to the N:P of non-fixing phytoplankton.

5 An additional mechanism not modelled herein is that phosphorite formation and consequent P removal from the ocean can be associated with fixed N removal due to denitrification (Piper and Codispoti, 1975; Schulz and Schulz, 2005). Qualitatively this acts in the right direction to further stabilise the deep ocean N:P ratio, although its effect will clearly depend on the (as yet unknown) proportions in which N and P are removed.

#### 10 4.1 Changes in deep ocean N:P over evolutionary time

The weathering flux of phosphorus to the ocean is thought to have increased with the biological colonisation of the land surface over the past 1000 Myr. Although this would have had some effect on ocean PO<sub>4</sub>, its dominant effect is predicted to have been an increase in ocean NO<sub>3</sub>, caused by increasing atmospheric O<sub>2</sub> and consequently suppressing denitrification. Thus, a reduction in phosphorus weathering alone ~1000 Ma would have tended to reduce the deep ocean N:P ratio (Fig. 8).

Our model of the effects of changes in weathering is quite simplistic. The scavenging of P by iron oxides in an oxygenated ocean may be more effective than modelled. Also, the organic C/P burial ratio may increase with anoxia (Van Cappellen and Ingall, 1996; 20 Lenton and Watson, 2000). Both processes provide negative feedback on changes in atmospheric oxygen. Including the latter process in the LW model tends to maintain higher O<sub>2</sub> and lower PO<sub>4</sub> under reductions in weathering, but does not alter the NO<sub>3</sub> prediction (Lenton and Watson, 2000). Consequently, the deep ocean N:P ratio tends to drop less under a reduction in weathering, but it still drops.

25 In contrast, members of phytoplankton groups that were present ~1000 Ma have higher N:P and C:P than today's average Redfield ratios (Quigg et al., 2003). Hence these organisms do not appear to have simply adapted to the estimated oceanic conditions at the time they evolved (consistent with Redfield's (1958) interpretation of the

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situation today). Instead, they are predicted to have altered those conditions: The higher N:P and C:P Redfield ratios  $\sim 1000$  Ma would have tended to decrease  $\text{PO}_4$  and hence increase the deep ocean N:P ratio (Table 3).

5 The combined effects of reduced weathering and increased N:P and C:P Redfield ratios in the mid-Proterozoic  $\sim 1000$  Ma may have been to maintain a similar deep ocean N:P ratio to today (Sect. 3.7). The lower  $\text{PO}_4$  predicted is consistent with much lower  $\text{PO}_4$  in the early Proterozoic 1900 Ma, followed by a rise in  $\text{PO}_4$  due to less removal on iron oxides (Bjerrum and Canfield, 2002). Over the past 1000 Myr, the suggested decline in N:P and C:P Redfield ratios (Quigg et al., 2003) would have driven an increase  
10 in  $\text{PO}_4$ , whilst the increase in phosphorus weathering and atmospheric  $\text{O}_2$  would have primarily driven an increase in  $\text{NO}_3$ . The net effect may have been (fortuitously) to maintain a relatively constant deep ocean N:P ratio.

## 4.2 Co-evolution?

We have extended Redfield's (1958) argument for the present ocean by adding an evolutionary time dimension, suggesting that over the last  $\sim 1000$  Myr, the composition of the marine environment has been altered by evolutionary changes in the composition of marine organisms, and by the biological colonisation of the land surface. This (and the modelling herein) describes a one-way interaction; biotic factors altering abiotic factors. However, phytoplankton composition may also adapt (within limits) to the composition  
20 of the ocean, which introduces the reverse interaction; abiotic factors shaping biotic factors. We have not modelled this here, but we acknowledge that it could qualitatively alter the results. Closing the loop between changes in biotic and abiotic factors would allow them to "co-evolve". To examine such co-evolution we suggest that a model of competing populations with differing stoichiometry could be nested within a model of  
25 ocean composition subject to external drivers. The populations themselves could exhibit phenotypic plasticity in their stoichiometry as their resource allocation varies in response to prevailing conditions (Klausmeier et al., 2004). This is a topic for future work.

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## 5 Conclusions

Despite potential changes in phytoplankton stoichiometry, weathering supply of phosphorus to the ocean, and widespread Fe and/or light limitation of  $N_2$ -fixation, we find that Redfield's mechanism can still regulate deep ocean N:P somewhat below the proportions that trigger  $N_2$ -fixation in those areas of the ocean where it is limited by P and suppressed by N addition. Furthermore, deep ocean N:P is unlikely to have varied by more than a factor of two in either direction since the deep oceans became well oxygenated. We extend Redfield's mechanism to suggest that within these bounds, the evolution of phytoplankton composition and the biological colonisation of the land surface could have driven long-term changes in ocean composition. Biotic stoichiometric controls on ocean composition could have operated much faster than phosphorus weathering controls, because they do not involve changes in atmospheric  $O_2$ .

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**Table 1.** Model parameters varied in this study and all remaining model constants.

Model	Class	Label	Description	Value
LW	Parameters	$W$	Normalised weathering forcing	1
		$r_{C:N}$	C:N Redfield ratio	117/16
		$r_{C:P}$	C:P Redfield ratio	117
		$r_{N:P}$	N:P Redfield ratio	16
		$r_{N:P,Fix}$	N:P threshold below which $N_2$ -fixation occurs	16
	Constants	$b_{C:N}$	Organic C:N burial ratio	37.5
		$b_{C:P}$	Organic C:P burial ratio	250
		$PO_{4(0)}$	Initial deep ocean phosphate concentration	$2.2 \mu\text{mol kg}^{-1}$
		$NO_{3(0)}$	Initial deep ocean nitrate concentration	$30.9 \mu\text{mol kg}^{-1}$
		$O_{2(0)}$	Initial oxygen concentration in ventilating water	$331.5 \mu\text{mol kg}^{-1}$
		$C_0$	Initial carbon concentration due to new production in surface waters	$226.0 \mu\text{mol kg}^{-1}$
		$k_P$	Initial $PO_4$ surplus in surface waters after $NO_3$ removal	$0.26875 \mu\text{mol kg}^{-1}$
		$A_0$	Initial anoxic fraction	0.14
		$k_1$	Initial oxic fraction	0.86
		$k_2$	Initial organic carbon burial flux	$3.75 \times 10^{12} \text{ mol C yr}^{-1}$
		$k_3$	Initial nitrogen fixation flux	$8.7 \times 10^{12} \text{ mol N yr}^{-1}$
		$k_4$	Half of initial denitrification flux	$4.3 \times 10^{12} \text{ mol N yr}^{-1}$
		$k_5$	Initial bio-available phosphorus input flux	$3.6 \times 10^{10} \text{ mol P yr}^{-1}$
		$k_6$	Initial iron-sorbed phosphorus burial flux	$0.6 \times 10^{10} \text{ mol P yr}^{-1}$
		$k_7$	Initial calcium-bound phosphorus burial flux	$1.5 \times 10^{10} \text{ mol P yr}^{-1}$
		$k_8$	Conversion factor from deep ocean reservoir size to concentration	$7.1 \times 10^{-22} \text{ kg}^{-1}$
		$k_9$	Conversion factor from atmospheric reservoir size to concentration	$8.96 \times 10^{-24} \text{ kg}^{-1}$
TT	Parameters	$R_{NF}$	N:P Redfield ratio of $N_2$ -fixers	16
		$R_O$	N:P Redfield ratio of other phytoplankton	16
		$f_A$	Fraction of surface ocean where $N_2$ -fixers can grow	1
		$f_B$	Fraction of surface ocean where $N_2$ -fixers cannot grow	0
	Constants	$P_H$	Half-saturation constant for growth on $PO_4$	$3 \times 10^{-5} \text{ mol P m}^{-3}$
		$N_H$	Half-saturation constant for growth on $NO_3$	$5 \times 10^{-4} \text{ mol N m}^{-3}$
		$\mu_{NF}$	Maximum growth rate for $N_2$ -fixers	$87.6 \text{ yr}^{-1}$
		$\mu_O$	Maximum growth rate for other phytoplankton	$91.25 \text{ yr}^{-1}$
		$M$	Mortality	$73 \text{ yr}^{-1}$
		$SD$	Depth of the surface layer	500 m
		$DD$	Depth of the deep layer	3230 m
		$K$	Mixing coefficient between the surface and the deep	$3.0 \text{ m yr}^{-1}$
		$SR$	Fraction of total primary productivity regenerated in the surface layer	95%
		$DN$	Fraction of total N uptake that is converted to $N_2$ via denitrification	1.5%
		$DR$	Fraction of total primary productivity regenerated in the deep layer	4.8%
		$RP$	River input of P	$2.0 \times 10^{-4} \text{ mol P m}^{-2} \text{ yr}^{-1}$
		$RN$	River input of N	$6.0 \times 10^{-3} \text{ mol N m}^{-2} \text{ yr}^{-1}$
		$AN$	Atmospheric input of N	$7.5 \times 10^{-3} \text{ mol N m}^{-2} \text{ yr}^{-1}$

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**Table 2.** Limits on ocean composition predicted from theoretical limits on the N:P stoichiometry of phytoplankton (Klausmeier et al., 2004) using the TT and LW models, and assuming in the latter that phytoplankton N:P is the N:P threshold that triggers N<sub>2</sub>-fixation.

Limit	Phytoplankton N:P	Predicted N:P of deep ocean		
		TT	LW with $r_{C:P}=117$	LW with $r_{C:N}=7.3$
Control	16	14.6	14.0	14.0
Exponential growth	8.2	8.1	7.2	7.7
Light limitation	35.8	31.3	31.4	27.3
N-limitation	37.4	32.7	32.8	28.2
P-limitation	45.0	39.1	39.5	32.3

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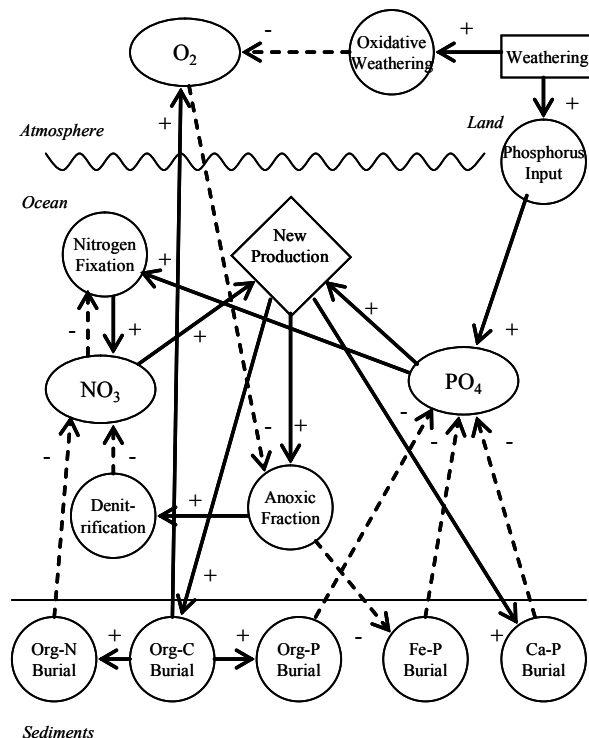
**Table 3.** Expected ocean composition if dominated by various phyla of phytoplankton. Predicted from the Redfield ratios found by (Quigg et al., 2003) and the adapted LW model, assuming the N:P Redfield ratio is the threshold below which N<sub>2</sub>-fixation occurs.

Phylum/superfamily (and age)	C:N:P ratio	NO <sub>3</sub> (μmol kg <sup>-1</sup> )	PO <sub>4</sub> (μmol kg <sup>-1</sup> )	NO <sub>3</sub> :PO <sub>4</sub>
Prasinophyceae (1200 Myr)	200:25:1	28	1.4	20
Chlorophyceae (1000 Myr)	200:33:1	38	1.4	27
Dinophyceae (440 Myr)	140:13:1	21	1.9	11
Prymnesiophyceae (210 Myr)	60:9:1	32	4.0	8.0
Diatoms (<200 Myr)	70:10:1	32	3.5	9.2

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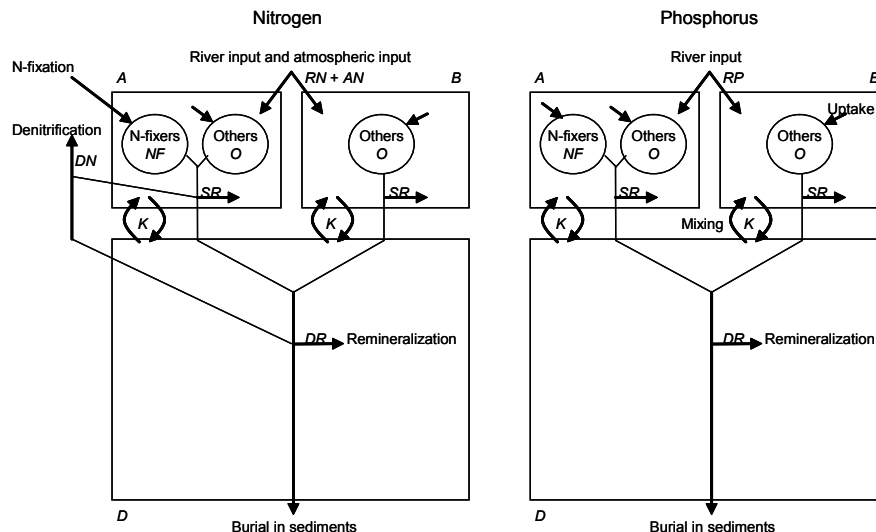
**Fig. 1.** Feedback diagram of the LW model where arrows indicate causal relationships. Ovals indicate reservoirs, circles indicate dependent variables, the diamond indicates a switch – new production is determined by either  $NO_3$  or  $PO_4$  – and the rectangle indicates the single input parameter, weathering. A solid arrow with a plus sign indicates a direct relationship, e.g. increased nitrogen fixation increases  $NO_3$ . A dashed arrow with a minus sign indicates an inverse relationship, e.g. increased  $NO_3$  decreases nitrogen fixation. In this example, a negative feedback loop is closed. All closed loops of arrows that can be traced around the diagram represent feedbacks. If there are an odd number of inverse relationships in a loop it is a negative feedback, whereas those containing none or an even number are positive feedbacks.

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**Fig. 2.** Schematics of the nitrogen and phosphorus cycles in the extended TT model, where arrows indicate fluxes. The model has two surface ocean boxes (*A*, *B*) and a deep ocean box (*D*). Within box *A* there are populations of nitrogen fixers and other phytoplankton. Within box *B* there are only other phytoplankton. Where possible, fluxes are labelled and model variables and constants are indicated in *italics*. Mixing (*K*) occurs between each surface box and the deep box but not between the two surface boxes. N enters the surface boxes from rivers (*RN*) and atmospheric deposition (*AN*). P enters from rivers (*RP*). Biological uptake of nutrient is indicated by an arrow from within a surface box to a population. N is also fixed from outside the system directly into the  $N_2$ -fixers. Mortality is represented by lines leaving the populations, forming sinking fluxes of nutrients. For both nutrients, a fraction (*SR*) of the sinking flux is remineralised in the surface layer and a fraction (*SD*) in the deep box. For N, a fraction (*DN*) is also lost by denitrification. The remaining sinking fluxes of nutrients leave the system as burial in sediments.

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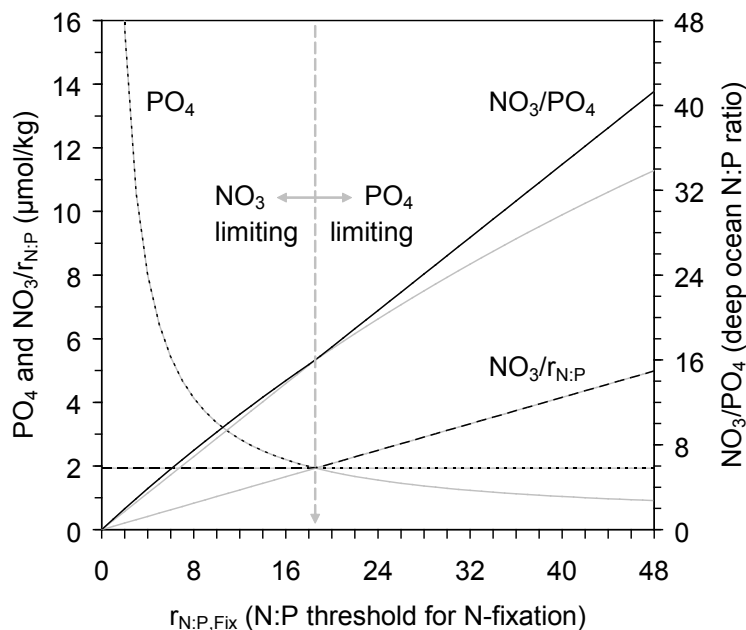
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**Fig. 3.** Analytic solutions for the dependence of steady state  $\text{PO}_4$  (dotted line),  $\text{NO}_3/r_{\text{N:P}}$  (dashed line), and deep ocean N:P ratio (solid line) on the N:P threshold for  $\text{N}_2$ -fixation ( $r_{\text{N:P,Fix}}$ ), in the LW model. Here the N:P Redfield ratio (i.e. the composition of all phytoplankton) is fixed at  $r_{\text{N:P}}=16$ . We plot  $\text{NO}_3/r_{\text{N:P}}$  rather than  $\text{NO}_3$  to visually indicate whether  $\text{PO}_4$  or  $\text{NO}_3$  is limiting. The pale grey solid lines show the solutions for both  $\text{NO}_3$  limiting and  $\text{PO}_4$  limiting conditions throughout. However, for a given value of  $r_{\text{N:P,Fix}}$ , only one set of solutions is valid and self-consistent. The space divides into two regimes, one where  $\text{NO}_3$  is limiting and the other where  $\text{PO}_4$  is limiting (when  $r_{\text{N:P,Fix}} \geq 18.6$ ).

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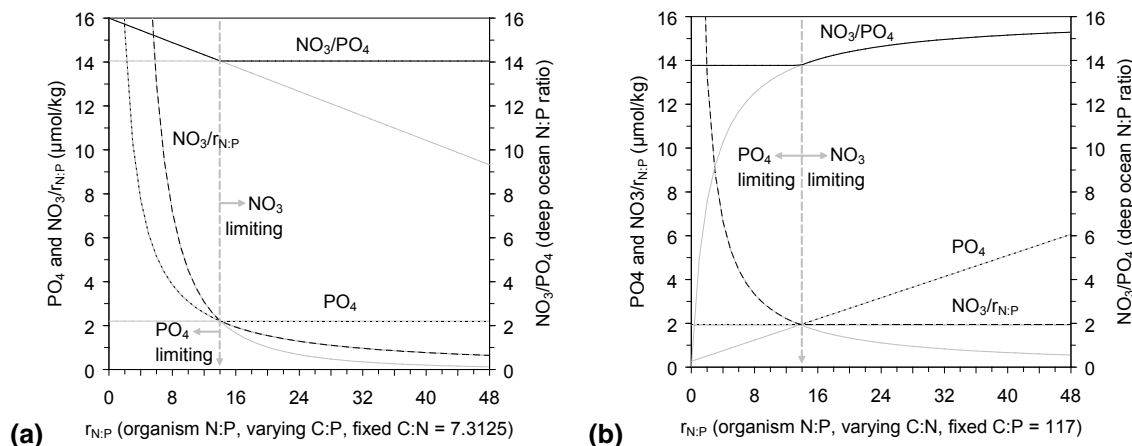
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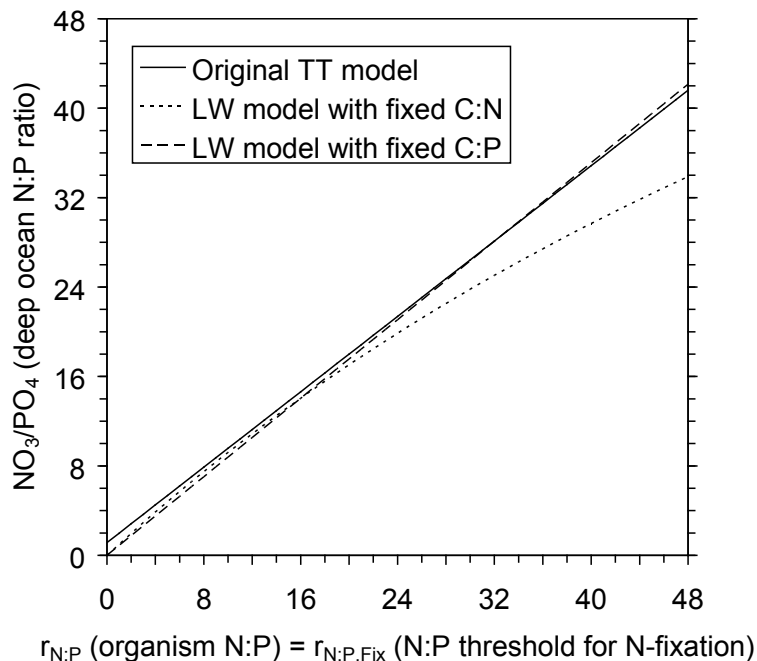


**Fig. 4.** Analytic solutions for the dependence of steady state  $\text{PO}_4$  (dotted line),  $\text{NO}_3/r_{\text{N:P}}$  (dashed line), and deep ocean N:P ratio (solid line) on the N:P Redfield ratio ( $r_{\text{N:P}}$ ), when the N:P threshold for  $\text{N}_2$ -fixation is fixed at  $r_{\text{N:P,Fix}}=16$ , in the LW model. **(a)** Fixing the C:N Redfield ratio at  $r_{\text{C:N}}=117/16=7.3125$ . Here in the N-limiting regime, deep ocean N:P=14.04, and a switch to  $\text{PO}_4$  limitation occurs when  $r_{\text{N:P}} \leq 14.04$ . **(b)** Fixing the C:P Redfield ratio at  $r_{\text{C:P}}=117$ . Here the switch to  $\text{PO}_4$  limitation occurs when  $r_{\text{N:P}} \leq 13.77$ , and this regime has deep ocean N:P=13.77. Other details are as in Fig. 3.

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**Fig. 5.** Analytic solutions for the dependence of the steady state deep ocean N:P ratio on the N:P Redfield ratio of the phytoplankton, when assuming that it determines the N:P threshold that triggers  $N_2$ -fixation ( $r_{N:P}=r_{N:P,Fix}$  in the LW model). For the original TT model (solid line), and the LW model when assuming either fixed C:N Redfield ratio ( $r_{C:N}=117/16=7.3125$ , dotted line) or fixed C:P Redfield ratio ( $r_{C:P}=117$ , dashed line).

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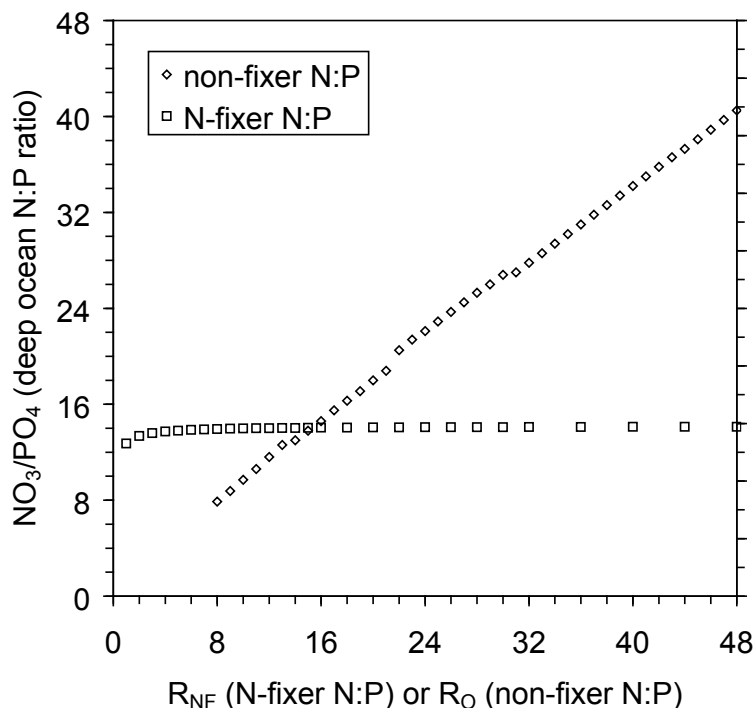
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**Fig. 6.** Numerical solutions for the dependence of the deep ocean N:P ratio on the N:P Redfield ratio of either  $N_2$ -fixing organisms,  $R_{NF}$  (squares) or other non-fixers,  $R_O$  (diamonds), in the extended TT model. When varying one Redfield ratio the other is held constant at 16. A stable steady state could not be found for  $R_O=7$  or less.

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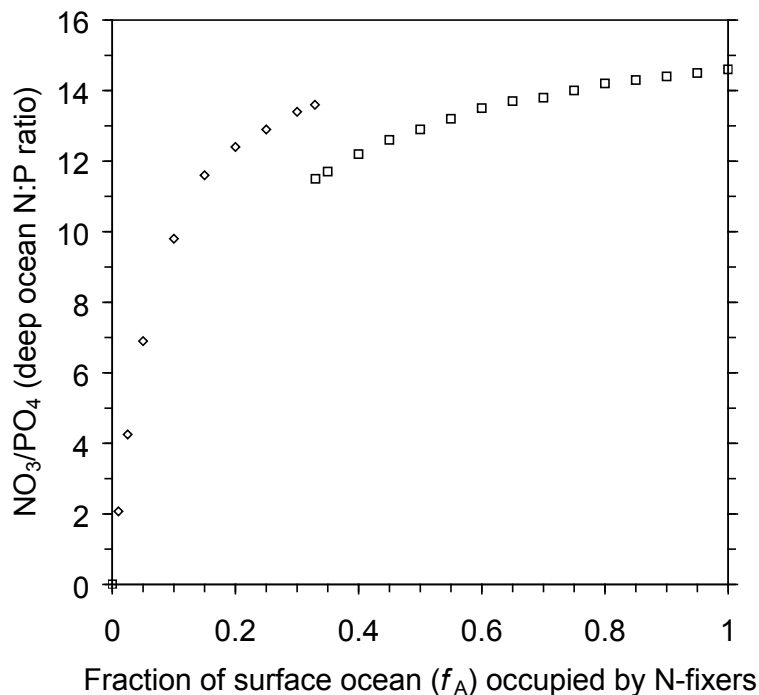
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**Fig. 7.** Dependence of the deep ocean N:P ratio on the fraction of the surface ocean occupied by  $N_2$ -fixers ( $f_A$ ) in the extended TT model, assuming an N:P Redfield ratio of 16 for both  $N_2$ -fixers and other phytoplankton. Square symbols indicate a stable solution, diamond symbols a limit cycle (oscillating solution). The oscillations are small, with a maximum amplitude of  $\sim 0.75\%$  (e.g. 13.3–13.5 for  $f_A=0.3$ ), and the diamonds are plotted at the mid point of the oscillations. The transition from a stable steady state to a limit cycle occurs in the range  $f_A=0.329$ – $0.330$ .

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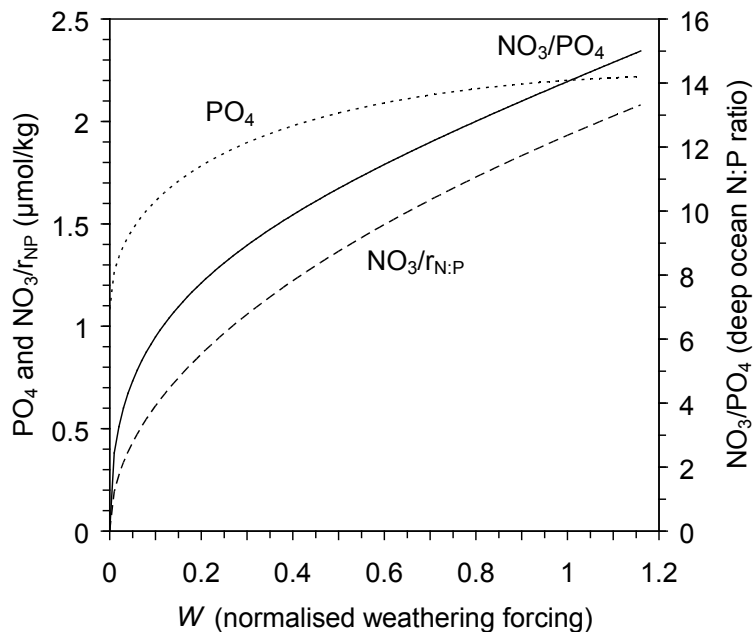
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**Fig. 8.** Analytic solutions for the dependence of steady state PO<sub>4</sub> (dotted line), NO<sub>3</sub>/r<sub>N:P</sub> (dashed line), and deep ocean N:P ratio (solid line) on weathering forcing ( $W$ ) in the LW model. Note that steady state is only achieved for  $W \leq 1.163$ .

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